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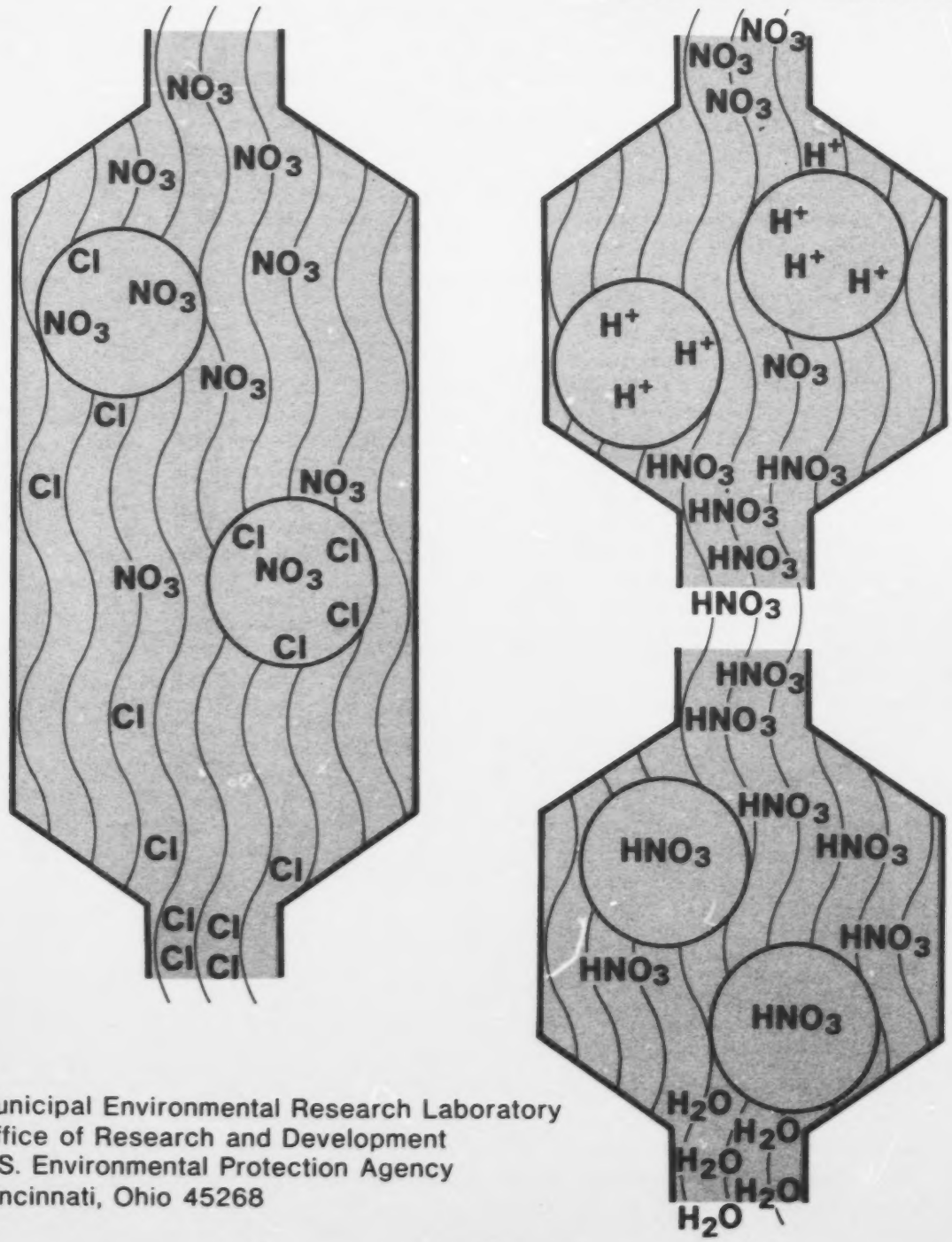
Executive Summary



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16. ABSTRACT

Anion exchange using synthetic organic resins is a proven and practical technology for the removal of nitrate from water supplies. However, disposal of the spent regenerant brime solution containing nitrate is a potential problem. Two processes were examined in detail in this report--single-bed strong-base anion exchange with NaCl regeneration and two-bed strong-acid, weak-base ion exchange with HCl and NH_4OH regeneration. Both systems must be operated to nitrate breakthrough to minimize regeneration costs. The two-bed process is one and one-half to two times as expensive to build and operate as is the single-bed process, but produces softened low-TDS, low-nitrate water, and has a readily disposable, spent regenerant with fertilizer value. Important design considerations were found to include the nitrate and sulfate concentrations in the raw water, the service flow rate, the resin bed depth, and the nitrate/chloride selectivity of the resin. The sulfate, nitrate, chloride, and bicarbonate selectivities and multicomponent column behavior of the anion resins available from U.S. manufacturers were examined and are reported in detail. An important peripheral finding was that significant quantities of non-volatile organics were leached from "clean" resins into the treated water.

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NITRATE REMOVAL FROM WATER SUPPLIES BY ION EXCHANGE

Executive Summary

by

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FOREWORD

The Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our natural environment. The complexity of that environment and the interplay between its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems for the prevention, treatment, and management of wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, for the preservation and treatment of public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research, a most vital communications link between the researcher and the user community.

Serious and occasionally fatal poisonings in infants have occurred following the ingestion of water containing high concentrations of nitrate. This report presents the results of an investigation on the removal of nitrate from water supplies by two-bed (strong-acid, weak-base) ion-exchange treatment systems and by single-bed (chloride form) ion-exchange systems. Detailed information is given on nitrate selectivity, rates, and capacities for nitrate and competing ions, and regeneration requirements for various commercially available anion-exchange resins. Also, an economic comparison is made between the single-bed and the two-bed ion-exchange systems.

Director Francis T. Mayo
Municipal Environmental Research Laboratory

ABSTRACT

Anion exchange using synthetic organic resins is a proven and practicable technology for the removal of nitrate from water supplies. However, disposal of the spent regenerant brine solution containing nitrate is a potential problem. Two processes were examined in detail in this report--single-bed strong-base anion exchange with NaCl regeneration and two-bed strong-acid, weak-base ion exchange with HCl and NH_4OH regeneration. Both systems must be operated to nitrate breakthrough to minimize regeneration costs. The two-bed process is one and one-half to two times as expensive to build and operate as is the single-bed process, but produces softened low-TDS, low-nitrate water, and has a readily disposable, spent regenerant with fertilizer value. Important design considerations were found to include the nitrate and sulfate concentrations in the raw water, the service flow rate, the resin bed depth, and the nitrate/chloride selectivity of the resin. The sulfate, nitrate, chloride, and bicarbonate selectivities and multicomponent column behavior of the anion resins available from U.S. manufacturers were examined and are reported in detail. An important peripheral finding was that significant quantities of non-volatile organics were leached from "clean" resins into the treated water.

This report was submitted in fulfillment of Grant No. R-803898 by the University of Michigan under the sponsorship of the U.S. Environmental Protection Agency. Work was completed as of December 31, 1976. A more complete report will be published at a later date.

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LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS (See glossary for definitions of terms)

BV	-	bed volumes
$CaCO_3$	-	Calcium Carbonate, 50 mg/meq
GEL	-	gel or microporous polymer
HCHO	-	formaldehyde
ID	-	inside diameter
Meq	-	milliequivalents, 10^{-3} gm equivalents
MR	-	macroporous polymer
NO_3-N	-	nitrate measured as nitrogen, mg/l
NVOC	-	non-volatile organic carbon, mg/l
POLY	-	polyamine functionality
Q-1	-	quaternary amine type 1 functionality
Q-2	-	quaternary amine type 2 functionality
Quat	-	quaternary amine functionality
STY-DVB	-	styrene-divinylbenzene polymer matrix
TDS	-	total dissolved solids, mg/l
tert	-	tertiary amine functionality
TOC	-	total organic carbon, mg/l
Typ	-	typical
VOC	-	volatile organic carbon, mg/l

SYMBOLS (see glossary for definitions of terms)

$\alpha_{N,Cl}$	-	the nitrate/chloride separation factor, dimensionless
α_{Cl}^{N}	-	the nitrate/chloride separation factor, dimensionless
$\alpha_{S,N}$	-	the sulfate/nitrate separation factor, dimensionless
α_{N}^{S}	-	the sulfate/nitrate separation factor, dimensionless
C_0	-	initial concentration of ion in water, meq/l
C_T	-	total concentration of ions in water, meq/l
Cl	-	chloride when used as a subscript
E_M	-	maximum possible chemical efficiency, dimensionless
E_0	-	overall chemical efficiency, dimensionless
E_R	-	regeneration efficiency, dimensionless
N	-	nitrate when used as a subscript
N	-	normality, qm equivalents/l
Q	-	ion-exchange capacity of resin, meq/ml
S	-	sulfate when used as a subscript
τ	-	superficial detention time, minutes
T	-	throughput, eq. of solution/eq. of exchanger
V_e	-	bed volumes of effluent to nitrate breakthrough
x_i	-	equivalent fraction of ion i in liquid, dimensionless
y_i	-	equivalent fraction of ion i on resin, dimensionless
$\bar{y}_N$	-	average equivalent fraction of nitrate on the resin, dimensionless, equals E_M
$\bar{y}_i$	-	average equivalent fraction of ion i on the resin, dimensionless

SECTION 1

INTRODUCTION

The maximum contaminant level (MCL) allowable for nitrate in community and non-community water supplies has been set at 10 mg/l as N in the Interim Primary Drinking Water Standards [19]. These standards were developed as a result of the Safe Drinking Water Act of 1974 and became effective on June 24, 1977. This nitrate level is equivalent to the long-standing, recommended limit established by the U.S. Public Health Service for the prevention of methemoglobinemia in infants; furthermore, the National Academy of Sciences [17] reported, in June of 1977 that, on the basis of available scientific information, there was no real justification for relaxing the MCL for nitrate. Public and private water supplies in nearly all of the fifty states, especially CA, NY, and TX, and in many foreign countries have been found to be polluted with nitrates in amounts regularly exceeding this 10 mg/l limit. Nitrate removal by ion exchange with synthetic, organic, anion-exchange resins is the treatment method which appears to offer the most readily available, proven technology at a cost which is lower than the alternatives -- reverse osmosis and electrodialysis. However, disposal of the spent nitrate-containing, regenerant-brine solution is an unsolved problem and, previous to the time of this research, there was a lack of technical information in the literature regarding the selectivity of the various anion exchange resins for nitrate with respect to the important ground water anions: chloride, sulfate, and bicarbonate. Neither was there sufficient, useful information available for the prediction of multicomponent effluent concentration profiles from ion-exchange columns economically operated by chromatographically eluting the ions not intended to be removed.

The research described here was undertaken to provide the missing data and to propose hypotheses concerning the prediction and control of anion exchange selectivity in general. A further objective was to provide a means of describing the multicomponent chromatographic column behavior of anion-exchange resins, especially weak-base resins, in nitrate removal service. A final objective was to perform technical and economic evaluations comparing a conventional, single-bed, strong-base, nitrate removal process to a two-bed, strong-acid, weak-base, nitrate removal process which would produce a spent ammonium nitrate regenerant amendable to disposal as a fertilizer.

SECTION 2

CONCLUSIONS

The preferences which commercially available anion exchangers exhibit for the common ground water anions varies drastically, especially in dilute multicomponent solutions with ions of differing valences. Nevertheless, these drastic differences do not translate simply into good or bad column performance in nitrate removal applications. Sulfate is always much preferred over nitrate and, below 3000 ppm TDS, the selectivity sequence for all commercially available resins is sulfate > nitrate > chloride >> bicarbonate. Strong and weak-base resins used for nitrate removal should be chosen on the basis of high nitrate/chloride selectivity not on the basis of low sulfate/nitrate selectivity. Surprisingly, high sulfate/nitrate selectivity actually improves the economics of nitrate removal in column operations.

The desirable anion resin characteristics for both single-bed and two-bed nitrate removal service are high nitrate/chloride selectivity, moderate to high sulfate/nitrate selectivity, moderate to high capacity, and macroporosity compared to microporosity. All thirty-two of the anion resins tested could be ranked in preference order for nitrate removal service but the differences among the recommended resins were only slight.

Ion-exchange system operating costs for single-bed and two-bed systems can often be reduced greatly by operating the anion bed to breakthrough of the ion intended to be removed (nitrate) rather than by operating to the ion-exchange capacity of the bed.

Kinetic considerations are important when eluting the ions not intended for removal. High service flow rates (> 2.5 gal/min. ft^3) and shallow beds (< 2 ft.) can result in premature breakthrough of the ion intended to be removed and in a resin loading favoring the faster ions not intended for removal.

Although predictably more costly to build and operate, feasible though complicated systems can be designed for nitrate removal applications which yield useful land-disposable regenerants.

The advantages (+) and disadvantages (-) of the single-bed and two-bed processes for nitrate removal are as follows:

Single-bed, strong-base anion with NaCl regeneration

(+) Simple, no balancing of beds and regenerants

(+) Low cost regeneration, typically 9¢/1000 gal. water supplied

(+) Lower capital cost compared to the two-bed process

(-) Very difficult and costly to dispose of regenerants in noncoastal locations where natural evaporation is impossible

(-) Iron must be removed to prevent resin fouling

(-) Continuous nitrate analysis required for process control

(-) Relatively high total operating costs, roughly 28¢/1000 gal. water supplied if no cost is assumed for regenerant disposal, and 37¢/1000 gal. water supplied assuming trucking and dilution disposal.

Two-bed, strong-acid, weak-base, HCl & NH_3 regenerants

(+) TDS reduction and partial softening in addition to nitrate removal

(+) No problem with iron fouling. Precipitated iron is removed from the cation bed during each regeneration cycle.

(+) Regenerant wastewaters expected to be easy to dispose of by land application as fertilizer

(-) Complex system: bed sizes and regenerants must be balanced

(-) Degasifier for CO_2 removal required

(-) Continuous pH and nitrate analysis required for process control

(-) High regenerant costs, typically 28¢/1000 gal. water supplied

(-) Higher capital costs compared to the single-bed process

(-) High total operating costs, roughly 55¢/1000 gal. water supplied with regenerants given away as fertilizer

The usual method of downflow exhaustion with downflow regeneration typically results in the need for 300 + % excess of regenerants for both strong acid and strong-base resins. The need for excess regenerants becomes greater whenever ions highly preferred by the ion exchanger (e.g., $SO_4^{=}$ for an anion exchanger and Ca^{++} for a cation exchanger) are involved. Although not specifically investigated in this research, countercurrent (upflow) regeneration can minimize the inefficient regeneration problem with its high costs for regenerant chemicals and their ultimate disposal.

All of the resins tested leached significant amounts of non-volatile organic matter into the treated water even after the resins were cleaned and conditioned. The total organic carbon (TOC) concentrations ranged from 3 to 90 mg/l for 1% resin solutions tumbled for 16 hours at 13 rpm and 25°C. Non-volatile organic carbon (NVOC) concentrations ranged from 61 to 3870 mg/l for the supernatant waters from 50% resin solutions left standing in distilled water for 6 months.

SECTION 3

RECOMMENDATIONS

The degree to which various cation and anion resins yield leachable organic compounds from breakdown of their polymer structures should be quantified and the compounds identified. These unwanted hydrocarbons are likely to be chlorinated during the traditional, water supply disinfection practices with the subsequent formation of possible carcinogenic compounds. The problem has some degree of urgency as the legal provisions of the 1974 Safe Drinking Water Act will necessitate the more widespread use of synthetic organic ion exchangers as the best available water treatment technology for removal of trace ionic contaminants, viz.: toxic metals, fluoride, and nitrate.

Pilot plant studies of the single-bed and two-bed ion-exchange systems described here should be undertaken to verify the cost estimates, assess the relative design, operation and control complexities, and evaluate the alternative means of regenerant disposal especially land application as a fertilizer.

Mathematical models for the prediction of nitrate breakthrough profiles should be developed based on the data presented here in conjunction with multicomponent chromatography theory.

Instrument research should be undertaken with the objective of developing a simple on-stream nitrate analyzer for monitoring nitrate in water supplies and in ion-exchange column effluents.

Polymer research should be undertaken with the objective of designing ion-exchange polymers which will be selective for monovalent-nitrate ions over divalent-sulfate ions based on the finding that the distance of nitrogen functional group separation is the most significant factor in univalent/polyvalent ion separations.

The anticipated, beneficial, catalytic effect of carbonic acid and bicarbonate ions on the nitrate removal efficiency of anion exchangers in multicomponent ion-exchange service should be investigated. Results of such an investigation should resolve the question of whether to place the system degasifier upstream or downstream of the anion exchanger.

SECTION 4

ION-EXCHANGE PROCESSES STUDIED

THE SINGLE BED PROCESS (Figure 1)

The "usual" [1, 8, 9, & 13] and conceivably the most economical means of nitrate removal from dilute solutions (<3000 mg/l TDS) using ion-exchange is a single-bed (fixed or moving) strong-base anion exchanger in the chloride form as described in Figure 1. With a typical ground water having the analysis shown, at least 25% of the feedwater may be safely bypassed and still provide a water of acceptable nitrate concentration (5--10 mg/l) right up until nitrate breakthrough. Offsetting the inherent economical advantages of the process are the following serious disadvantages.

(1) Resin selectivity for nitrate was originally though to be a potentially serious problem because sulfate was expected to be preferred with a selectivity ratio of more than 2/1 over nitrate.

(2) When present, ferrous iron oxidizes, precipitates, and seriously fouls the resin.

(3) Regeneration and brine disposal are the major economic and environmental problems yet to be solved even with low-cost NaCl regeneration.

THE TWO-BED STRONG-ACID WEAK-BASE PROCESS (Figure 2)

Because this two-bed process seemed to have certain advantages with respect to regeneration efficiency, iron removal, regenerant disposal as fertilizer and nitrate selectivity, the little-studied weak-base resin portion of the two-bed system shown in Figure 2 was examined in detail. The thermodynamic and kinetic data from the weak-base resin studies were compared and contrasted to the data obtained from strong-base resins of the type used in the single-bed process shown in Figure 1.

Evans [7] reported on a similar two-bed nitrate removal process, but with HCl and lime as the regenerants. His data indicated that, even after the cation bed was exhausted, and sodium was being eluted, the system continued to provide softening and nitrate removal thereby delivering greater than stoichiometric efficiency due to the weak-base anion resin's apparent selectivity for nitrate over all the other ions present including sulfate. Actually, in the total concentration range experienced with water supplies (100 to 5000 mg/l TDS), nitrate is thermodynamically <u>not</u> the most preferred

ion. The often reported sequence for both strong and weak-base resins is [1, 5, 6, 10 & 16]

sulfate > nitrate > chloride > bicarbonate

In this concentration range, both cation and anion exchangers of the synthetic organic resin type much prefer divalent over monovalent ions (although carbonate is an exception, it being less preferred than nitrate [16]). This preference for multivalent ions at low concentrations is referred to as "electroselectivity" [10]; it diminishes with increasing solution concentration, and in the cases of sulfate/nitrate and sulfate/chloride exchange, reverses to favor the monovalent ions at TDS concentrations above approximately 5000 mg/l as $CaCO_3$ [1, 3 & 15].

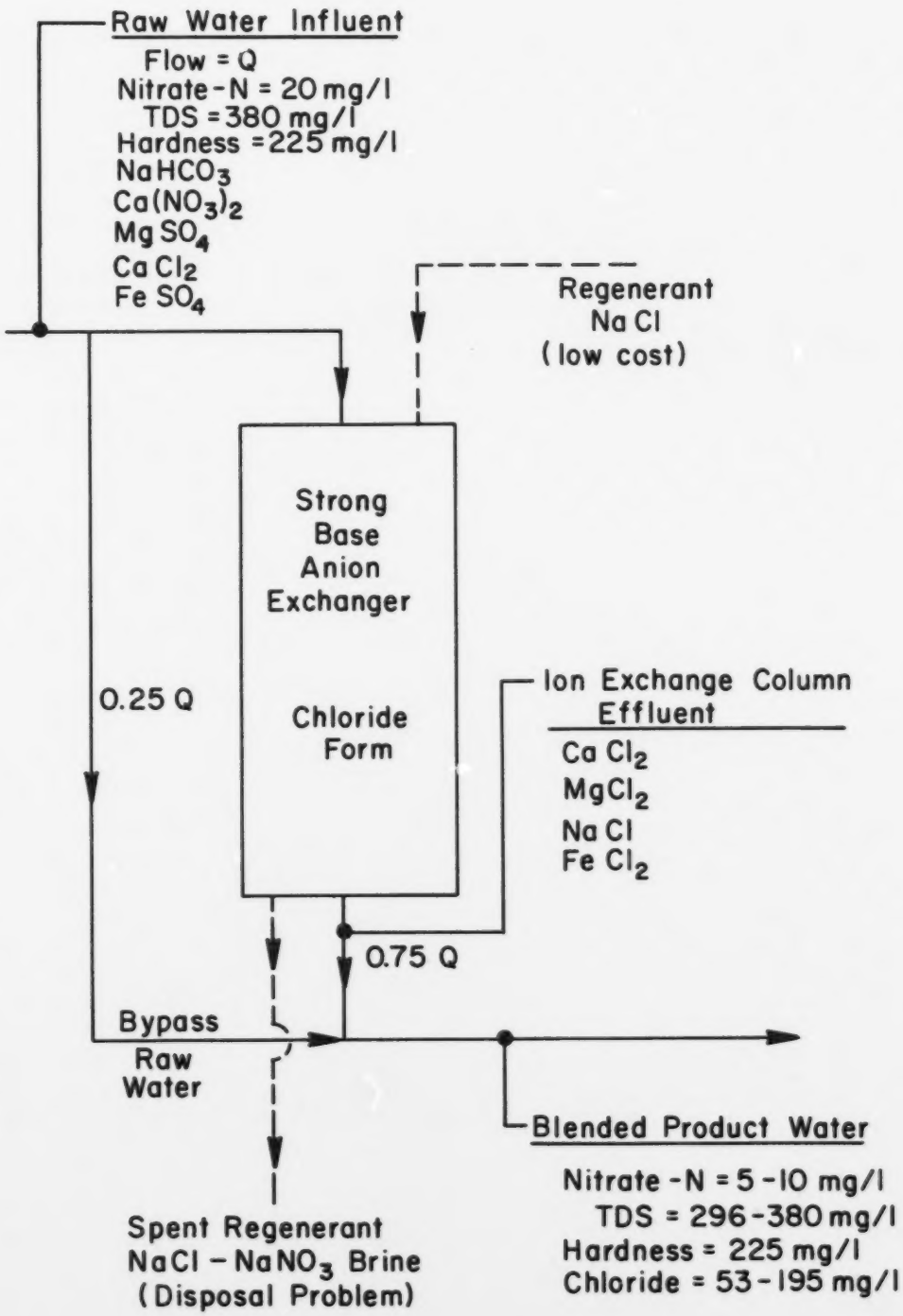


Figure 1 Conventional Single Bed Ion Exchange Process

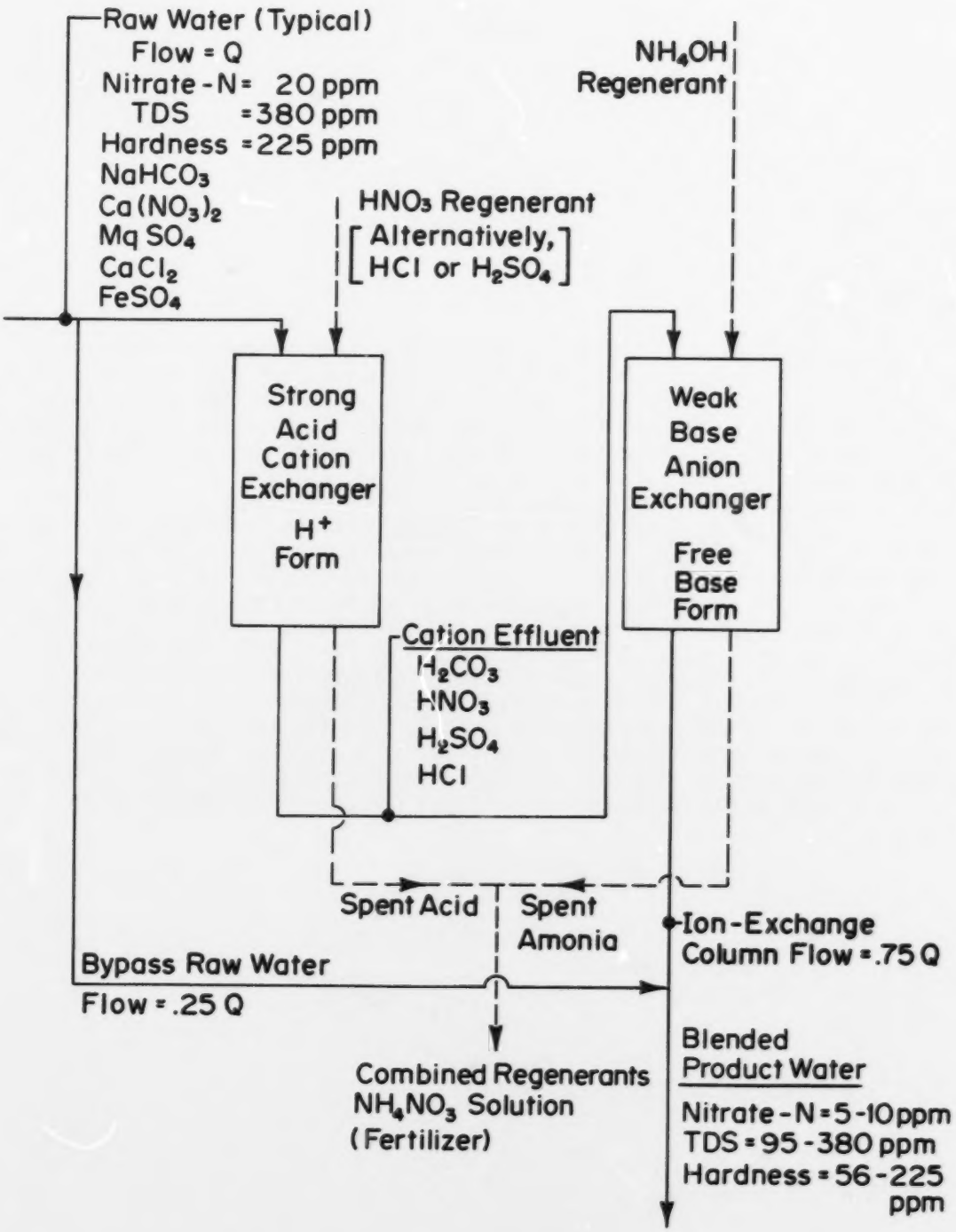


Figure 2 Proposed Two-Bed, Ion-Exchange Process

SECTION 5

EXPERIMENTAL PROCEDURES

THEORY

With experimentally determined separation factors, multicomponent chromatography theory [11, 12, 14 & 18] can be used with some simplifying assumptions to predict the resin-phase concentration profiles of the anion exchangers used in the single-bed and two-bed processes. The ions removed by the resin tend to become separated and concentrated into enriched zones containing predominantly one species as depicted in Figure 3. A hypothetical, semiquantitative profile based on the selectivity sequence given above showing the idealized distribution of sulfate, nitrate, chloride, and bicarbonate is given in Figure 4 for the case in which the feed water contains the same equivalent concentrations of the four anions shown. The most preferred species, sulfate, is removed preferentially and is concentrated near the inlet to the column. Bicarbonate, the least preferred species, is removed nearer to the exit end of the column and is the first ion other than the exchanging ion to show up in the effluent. Nitrate and chloride being of intermediate affinity are concentrated in zones between these two extremes. Quantification of the breakthrough curves for all the ions may be approximated if the selectivity coefficients (K's) or separation factors (α's) are known for the ions of interest [12, 14]. These constants are defined below for an example sulfate/nitrate ion-exchange reaction on a typical anion resin:

$$2\,\overline{RNO_3} + SO_4^{=} \rightleftarrows \overline{R_2SO_4} + 2NO_3^{-}$$

$$K_{S,N} = \begin{matrix}\text{Sulfate/Nitrate} \\ \text{Selectivity Coefficient}\end{matrix} = \frac{[\overline{R_2SO_4}]\,[NO_3^{-}]^2}{[SO_4^{=}]\,[\overline{RNO_3}]^2}$$

$$\alpha_{S,N} = \begin{matrix}\text{Sulfate/Nitrate} \\ \text{Separation Factor}\end{matrix} = \frac{y_S}{x_S} \Big/ \frac{y_N}{x_N}$$

$$K_{S,N} = \alpha_{S,N}\,\frac{C_0}{Q}\,\frac{x_N}{y_N}$$

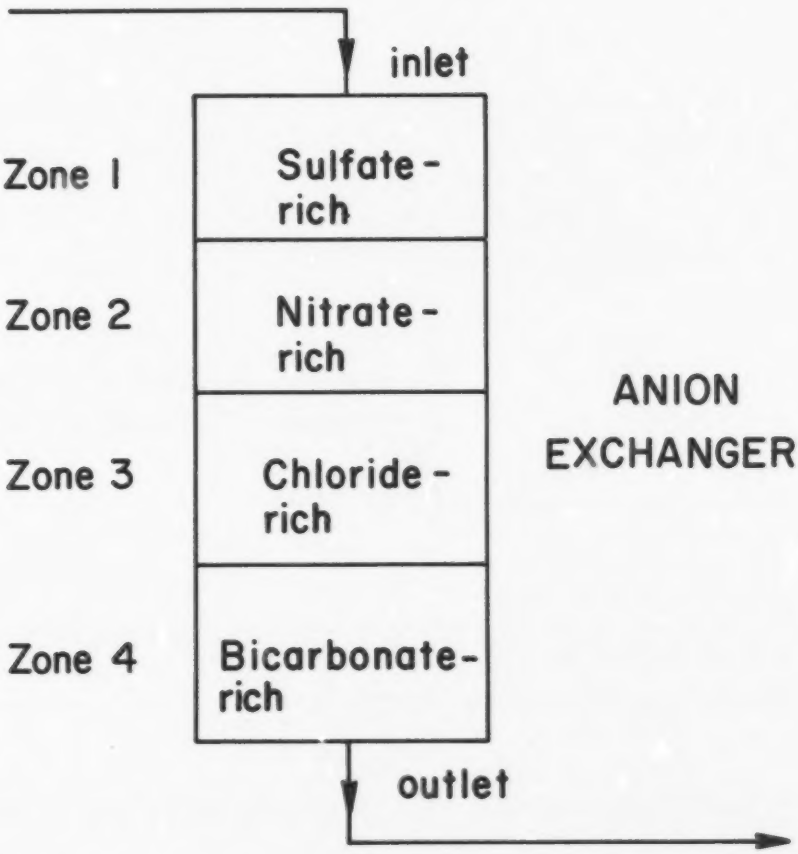


FIGURE 3

Chromatographic Enrichment of Ground Water Anions in an Exhausted Anion Exchanger

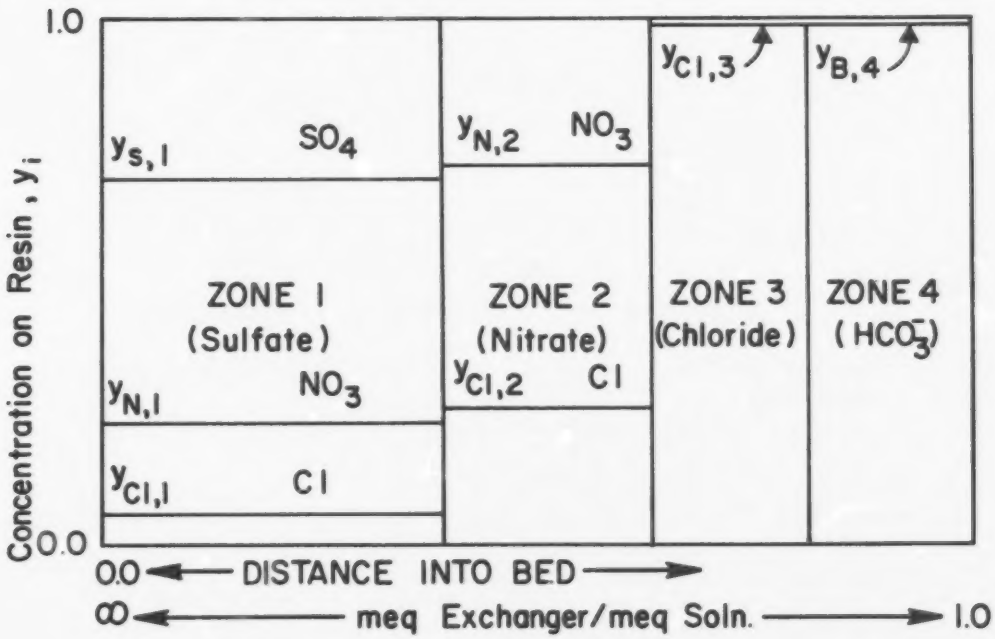


FIGURE 4

HYPOTHETICAL RESIN PHASE CONCENTRATION PROFILE

$y_{Cl,i}$ = eq. fraction of chloride in zone i

$y_{S,1}$ = eq. fraction of sulfate in zone 1

$y_{N,1}$ = eq. fraction of nitrate in zone 1

$y_{N,2}$ = eq. fraction of nitrate in zone 2

$y_{B,4}$ = eq. fraction of bicarbonate in zone 4

where: R = ion-exchange site on resin

$\overline{R_2SO_4}$ = sulfate in the resin phase

$SO_4^=$ = sulfate in the liquid phase (water)

[ ] = denotes concentration in eq/l

y_S = equivalent fraction sulfate on the resin

x_S = equivalent fraction sulfate in the water

C_0 = Total conc. of liquid phase in eq/l

Q = Total capacity of the resin in eq/l

Separation factors and selectivity coefficient can be determined from (isothermal) plots of resin phase concentration vs. water phase concentration of the ions being exchanged -- binary ion-exchange isotherms. One important objective of the research was to develop sulfate/nitrate and chloride/nitrate isotherms for all the commercially available strong and weak-base anion exchangers manufactured in the U.S. Column two of Table 1 contains a listing of all the resins evaluated during the research study.

SELECTIVITY STUDIES

The experimental sulfate/nitrate isotherms were constructed by equilibrating (for 16 hrs.) weighed samples of resins in the nitrate form with 0.005 N H_2SO_4 (250 mg/l as $CaCO_3$) solutions and measuring the redistribution of ions, i.e., ion exchange, which took place. At least five data points were obtained for the construction of each isotherm with each of the 32 resins. Nitrate/chloride isotherms were constructed for 20 of the resins by equilibrating weighted samples of resins in the nitrate form with 0.005 N HCl (250 mg/l as $CaCO_3$). Some examples of sulfate/nitrate and nitrate/chloride isotherms are given in Figures 5-7. Bicarbonate/nitrate selectivity studies were also conducted on 12 of the resins utilizing a similar technique in a closed system to prevent the escape of CO_2.

ION EXCHANGE COLUMN STUDIES

After a preliminary evaluation of the binary equilibrium data, resins were selected for laboratory scale (1" ID by 24" deep) column experiments in which the chromatographic elution of ions was to be observed and hopefully quantified with the help of the experimentally determined separation factors. A simulated ground water (See Table 2) was used in most of these studies. Ten of the eleven multicomponent column runs were made with the two-bed system described in Figure 2 as simulated by the experimental flow system shown in Figure 8. One comparison run was made with the single-bed system described in Figure 1 by simply bypassing the cation column shown in Figure 8. Complete experimental details, results, and analysis for both the selectivity and column studies can be found in Reference 4.

TABLE 1: ANION RESIN CHARACTERISTICS

UM Resin Number	Manufacturer's Designation	Matrix	Functionality	Porosity	meq/ml Advertised Capacity	meq/ml Measured HCl Capacity	pKa	Average α_N^S	Average α_{Cl}^N
15	AMBERLITE IRA-400	STY-DVB	Q-1	MICRO	1.40	1.53	>13	1.89	-
17	AMBERLITE IRA-900	STY-DVB	Q-1	MACRO	1.00	1.10	>13	1.71	3.41
21	DOWEX SBR	STY-DVB	Q-1	MICRO	1.40	1.66	>13	1.89	2.90
27	IONAC ASB-1	STY-DVB	Q-1	MICRO	1.40	1.39	>13	1.87	-
32	IONAC AFP-100	STY-DVB	Q-1	MACRO	1.20	1.07	>13	1.76	2.97
16	AMBERLITE IRA-400	STY-DVB	Q-1	ISO	1.25	1.16	>13	3.09	3.11
19	DOWEX SBR-P	STY-DVB	Q-1	ISO	1.20	1.02	>13	2.96	-
22	DOWEX 11	STY-DVB	Q-1	ISO	1.20	1.17	>13	3.37	-
24	DUOLITE A-101-D	STY-DVB	Q-1	ISO	1.30	1.32	>13	2.59	-
28	IONAC A-641	STY-DVB	Q-1	FM	1.16	1.21	>13	3.30	3.30
30	IONAC ASB-1P	STY-DVB	Q-1	ISO	1.35	1.13	>13	2.59	-
14	AMBERLITE IRA-910	STY-DVB	Q-2	MACRO	1.00	1.31	>13	3.26	2.85
18	AMBERLITE IRA-410	STY-DVB	Q-2	MICRO	1.35	-	>13	2.40	-
20	DOWEX SAR	STY-DVB	Q-2	MICRO	1.40	1.50	>13	3.04	-
23	DUOLITE A-102-D	STY-DVB	Q-2	MICRO	1.40	1.48	>13	3.26	-
29	IONAC ASB-2	STY-DVB	Q-2	MICRO	1.52	1.33	>13	3.04	3.64
1	AMBERLITE IRA-93	STY-DVB	TERTIARY	MACRO	1.25	0.98	7.7	3.75	4.86
5	DOWEX MWA-1	STY-DVB	TERTIARY	MACRO	1.10	1.15	7.6	2.67	4.43
8	DUOLITE ES-368	STY-DVB	TERTIARY	MACRO	1.30	1.43	7.8	2.83	3.87
12	IONAC AFP-329	STY-DVB	TERTIARY	MACRO	1.25	1.26	8.5	3.07	4.14
3	AMBERLITE IR-45	STY-DVB	POLY	MICRO	1.90	1.76	7.9	12.7	3.89
2	AMBERLITE IRA-68	ACRYLIC-AMINE	TERTIARY	MICRO	1.60	1.42	11.1	23.4	1.89
10	DUOLITE ES-374	ACRYLIC-AMINE	POLY*	MACRO	3.0	2.59	9.9	94.0	3.85
6	DUOLITE A-7	PHENOL-HCHO-PA	POLY**	MACRO	2.4	1.67	7.7	108	3.35
9	DUOLITE ES-561	PHENOL-HCHO-PA	POLY	MACRO	2.0	1.22	6.8	109	2.65
11	IONAC A-260	ALIPHATIC-AMINE	POLY	MICRO	1.8	1.81	10.6	54.0	2.25
4	DOWEX WGR	EPOXY-AMINE	POLY	MICRO	1.0	1.53	7.9	137	1.99
7	DUOLITE A-340	EPOXY-AMINE	POLY	MICRO	2.6	2.54	8.7	82.9	1.70
13	IONAC A-305	EPOXY-AMINE	POLY+	MICRO	3.5	1.51		108	-

POLY = Polyamine not including quaternary amine
Q-1 = Quarternary Amine - Type 1
Q-2 = Quarternary Amine - Type 2
ISO = Isoporosity or "Improved Porosity"
FM = Fixed Macropore (MANUFACTURER'S TERMINOLOGY)

POLY* = Advertised as tertiary amine but titrates as polyamine
POLY** = Advertised as secondary amine but titrates as polyamine
POLY+ = Polyamine including quaternary amine

TABLE 2: COMPOSITION OF SIMULATED GROUND WATER

Ion	X_i	meq/l	mg/l
Cations			
Ca^{++}	.546	3.0	60
Mg^{++}	.273	1.5	18
Na^{+}	.181	1.0	23
Fe^{++}	nil	nil	1
Total Cations	1.00	5.5	102
Anions			
$SO_4^{=}$	.273	1.5	72
NO_3^{-}	.273	1.5	93
Cl^{-}	.273	1.5	53
HCO_3^{-}	.181	1.0	61
Total Anions	1.00	5.5	279

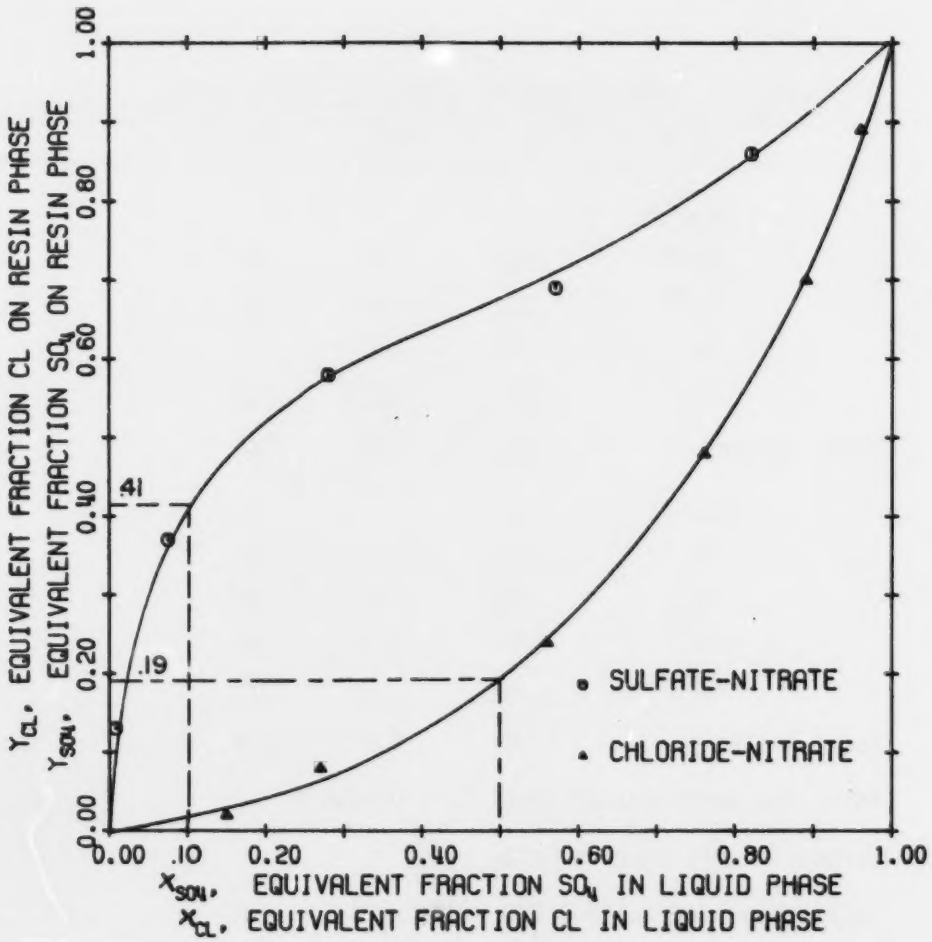
Total Concentration of ions, C_T = 0.0055 N

Hardness = 225 mg/l as $CaCO_3$

Total dissolved solids, TDS = 381 mg/l

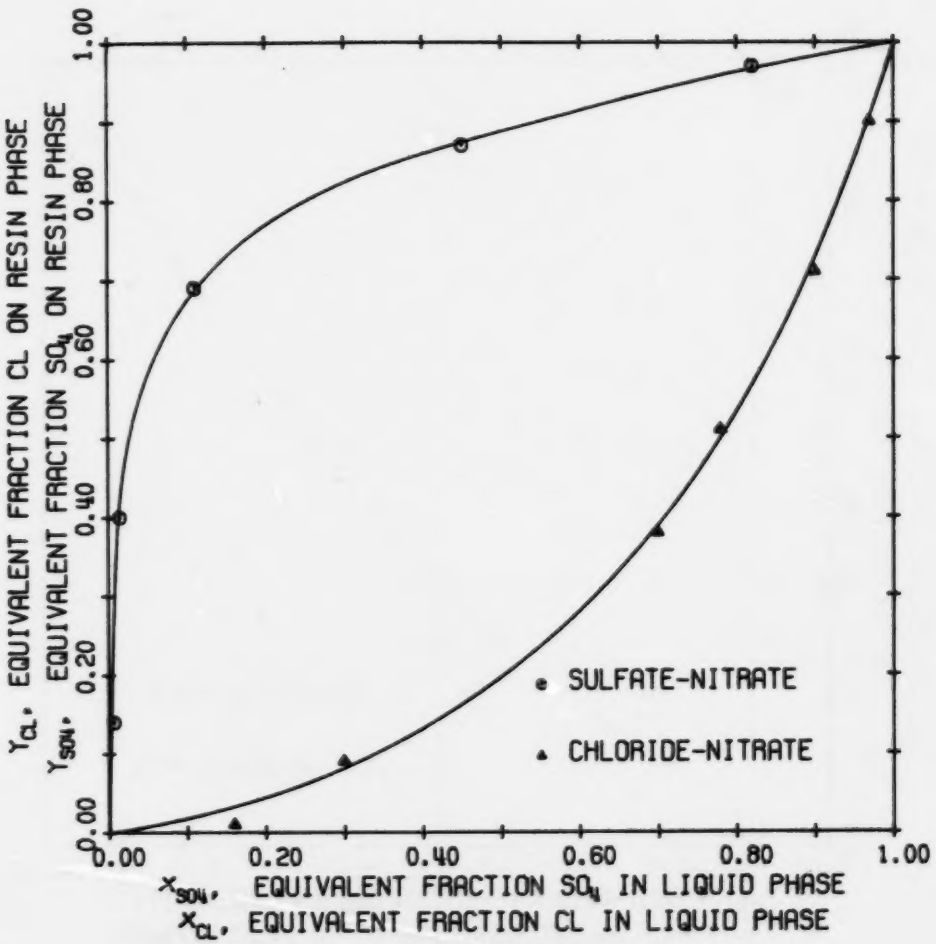
Nitrate as nitrogen, NO_3-N = 21 mg/l

Equivalent fraction of nitrate, x_N = 0.27



RESIN NUMBER 8
DUOLITE ES 368, MACROPOROUS RESIN
STYRENE-DVB MATRIX
TERTIARY-AMINE FUNCTIONALITY
TOTAL CAPACITY=1.3 MEQ/ML

FIGURE 5
25° C, BINARY ION-EXCHANGE ISOTHERM



RESIN NUMBER 3
AMBERLITE IR 45, MICROPOROUS GEL
STYRENE-DVB MATRIX
POLYAMINE FUNCTIONALITY
TOTAL CAPACITY=1.9 MEQ/ML

FIGURE 6
25° C, BINARY ION-EXCHANGE ISOTHERM

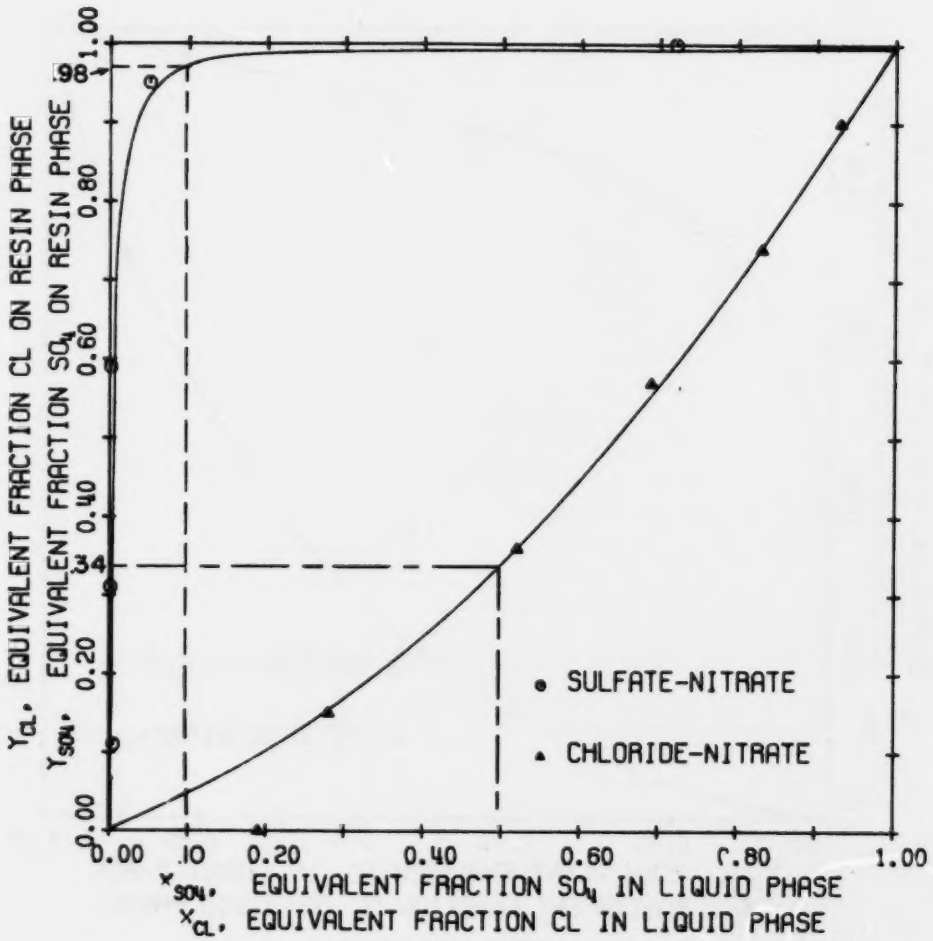


FIGURE 7
25° C, BINARY ION-EXCHANGE ISOTHERM

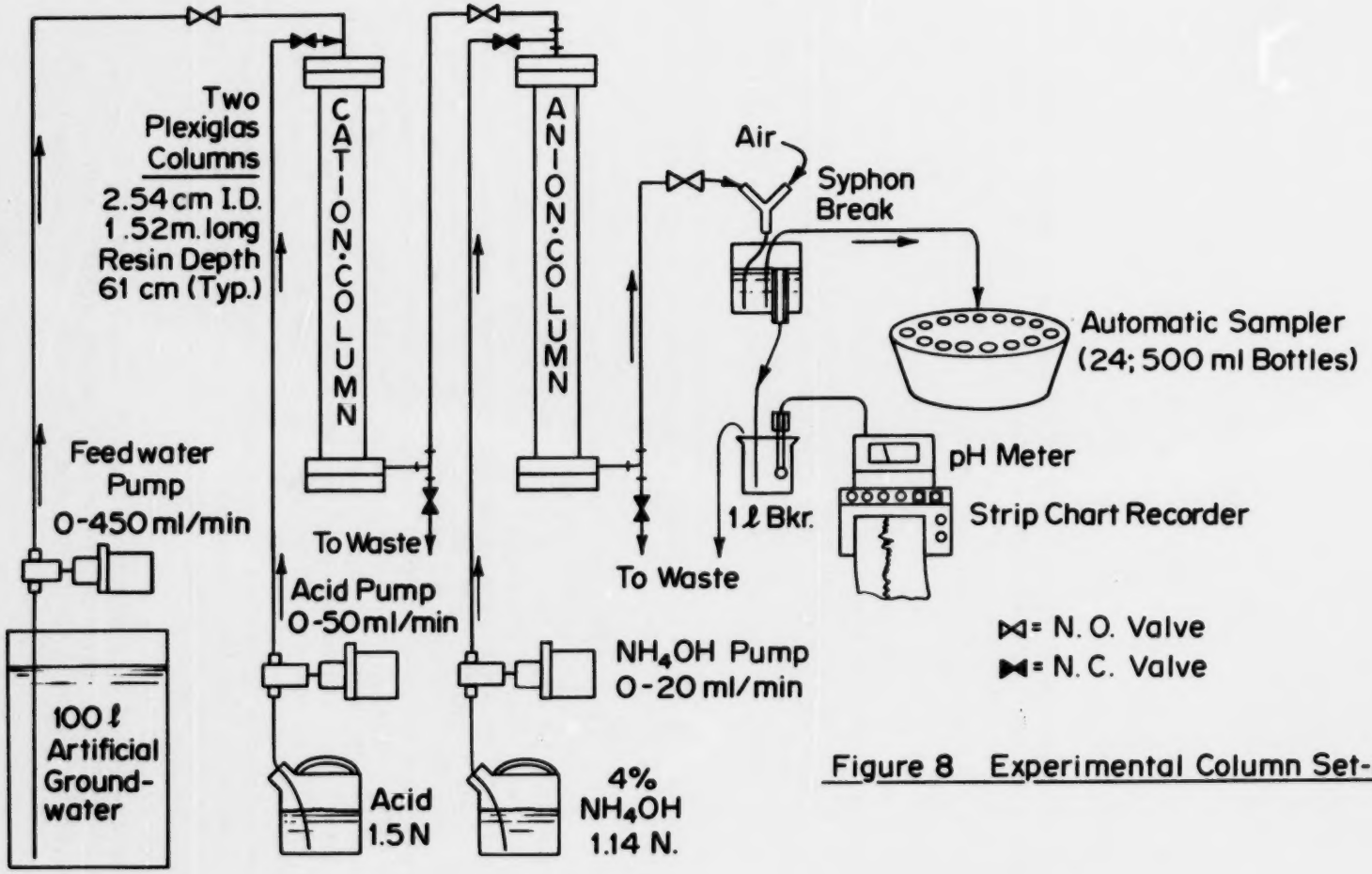


Figure 8 Experimental Column Set-up

SECTION 6

DISCUSSION OF RESULTS

RESIN SELECTIVITIES

All nineteen strong-base and thirteen weak-base resins commercially available from American manufacturers were tested for sulfate, nitrate, chloride, and bicarbonate selectivities. These selectivities were then related to the following resin properties: matrix, functionality, porosity, capacity, basicity, and type. A significant finding was that resin matrix is the most influential factor in the determination of divalent/monovalent selectivities. It is hypothesized that if many pairs of closely spaced ion-exchange sites are present in the resin matrix then the resin is very divalent ion selective. High divalent selectivity can be designed into a resin first by choosing the proper resin polymer structure (non-polystyrene > polystyrene) and second by selecting the proper functionality (primary > secondary > tertiary > quaternary amine). See Reference 4 for details.

Sulfate was always preferred over nitrate by all the strong and weak-base resins tested which exhibited an extremely wide range of selectivities: $\alpha_{S,N}$ = 1.71--3.37 for strong-base resins and 2.67--137 for weak-base resins. (Note: The larger is $\alpha_{S,N}$ the greater is the resin preference for sulfate over nitrate.) It is expected that the sulfate preference observed will hold true for any resin tested with feed waters having total dissolved solids concentrations up to at least 0.06 N (3000 mg/l as $CaCO_3$). Example isotherms for moderately (Figure 5) strongly (Figure 6) and very strongly (Figure 7) sulfate-selective resins are given for comparison purposes. The uppermost, convex, curve in each figure depicts the sulfate/nitrate equilibrium relationship for that resin. The degree of curvature exhibited by the isotherm indicates the resin's preference for sulfate over nitrate. Compare Figures 5 and 7: when x_S = 0.10, y_S = 0.41 for resin No. 8 (Figure 5) while y_S = 0.98 for resin No. 4 when x_S = 0.10. In other words, when sulfate represents 10% of the negative ionic charges in the equilibrium aqueous phase, 41% of the resin phase exchange sites are occupied by sulfate in the moderately sulfate selective resin No. 8 (Figure 5) while 98% of the exchange sites are occupied by sulfate in the very strongly sulfate selective resin No. 4 (Figure 7). In both examples, the sites not occupied by sulfate are occupied by nitrate, as these isotherms were derived from binary, sulfate-nitrate mixtures.

Nitrate was always preferred over chloride by all the anion resins tested although the range of preferences was relatively narrow: $\alpha_{N,Cl}$ = 2.85--3.64 for strong-base resins and 1.70--4.86 for weak-base resins.

As expected, $\alpha_{N,Cl}$ was independent of total solution concentration. The chloride/nitrate isotherms, the lower curves in Figures 5--7, demonstrate a weak nitrate preference (Figure 7) and moderate nitrate preferences (Figures 5 and 6).

Bicarbonate and carbonic acid are not significantly taken up by ion-exchange resins in binary equilibrium with NO_3^- and HNO_3. The expected selectively sequence has been verified as sulfate > nitrate > chloride >> bicarbonate. Table 1 summarizes the selectivity characteristics of all the anion resins studied during the course of this research. When using the selectivities, as measured by the separation factors listed in Table 1, note that the sulfate/nitrate selectivities are strictly valid only at a total ionic concentration of 0.005 N (250 ppm as $CaCO_3$) while the nitrate/chloride selectivities are independent of total ionic concentration.

MULTICOMPONENT EFFLUENT PROFILES

The curves depicting the effluent concentration vs. bed volumes of treated effluent for all eleven runs are typified by Figure 9, a two-bed run, and Figure 10, the single-bed run. Consider Figure 9 (Run 11) as typical of the general effluent behavior of the four anions of interest and note that, as predicted from multicomponent chromatography theory, there are four plateaus each corresponding to a maximum concentration of one of the anions, and that these plateaus are separated by rather abrupt transition zones. The first component to appear is always H_2CO_3 or HCO_3^- followed by Cl^-, NO_3^-, and finally $SO_4^=$, the most preferred species. Observe also that, as expected, all species except for the most preferred species (sulfate) appear at some time in the effluent in concentrations from 130--350% of their concentrations in the feed water. An abrupt increase in the concentration of one component in the effluent is always accompanied by a correspondingly abrupt concentration decrease in a second component once the H_2CO_3 has been eluted. The single-bed effluent profile (Run 7, Fig. 10) differs from the two-bed profile (Figure 9) in that the strong-base anion bed was presaturated with Cl^-, the exchanging ion, which was always present in the effluent; nevertheless, the same general effluent behavior of the anions prevails.

Upon examination of the chloride and nitrate breakthrough curves from the two-bed run in Figure 9 it is noted that by not terminating the run on conductivity breakthrough (Cl^- breakthrough) the capacity of the bed in terms of bed volumes of effluent treated is increased from 320 to 480 bed volumes (V_e). This is a 50% efficiency increase and is due to elution of species less preferred than nitrate. In Figures 9 and 10, C_0's indicate the influent concentrations in meq/l of each of the anions; the complete test water composition is detailed in Table 2. Nitrate breakthrough has been defined as 0.48 meq/l of nitrate or 6.7 mg/l of nitrate-N. At that time the composition of the blended water will have reached the maximum permissible concentration of 10 mg/l.

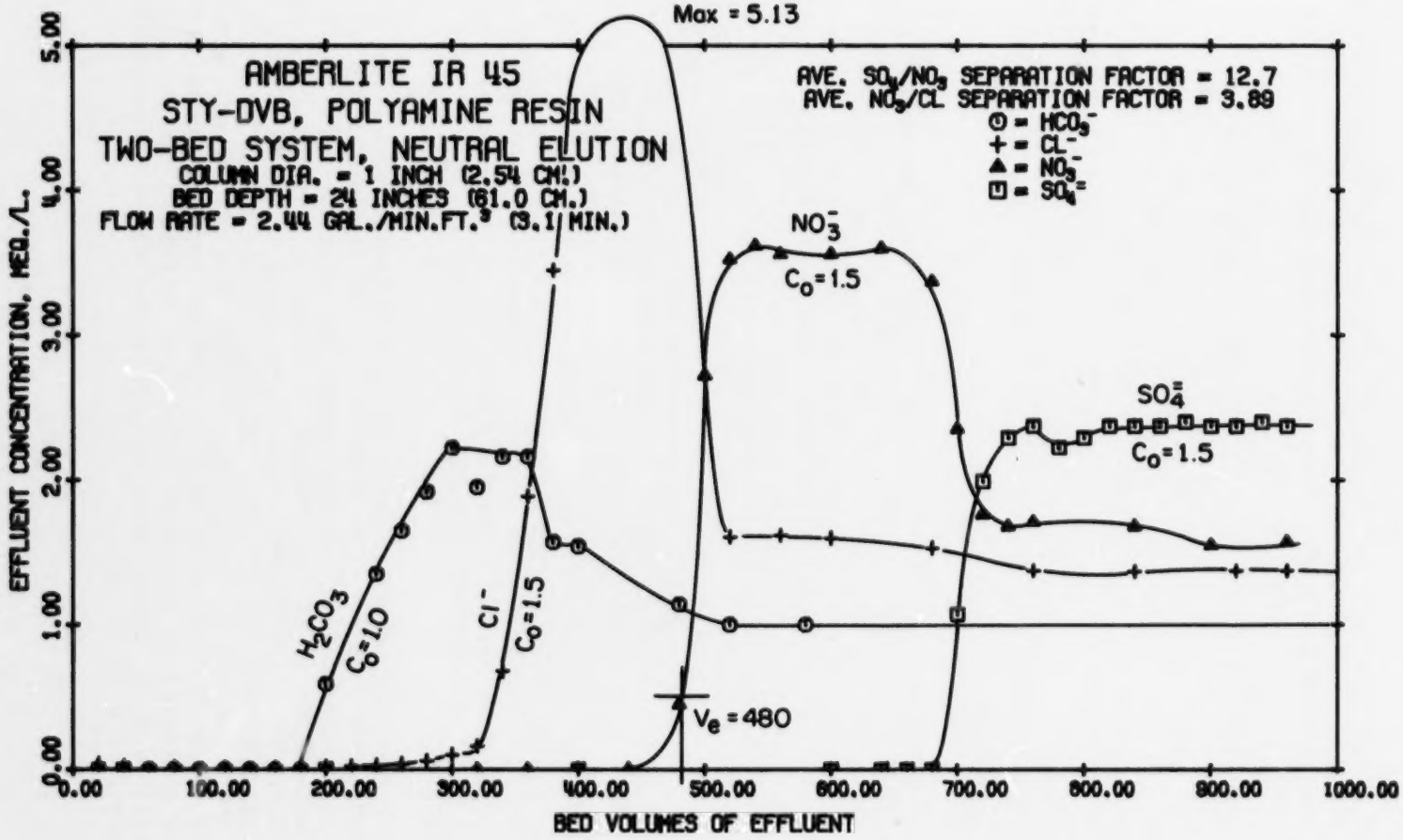


FIGURE 9
RUN NO. 11, EFFLUENT CONCENTRATION PROFILE

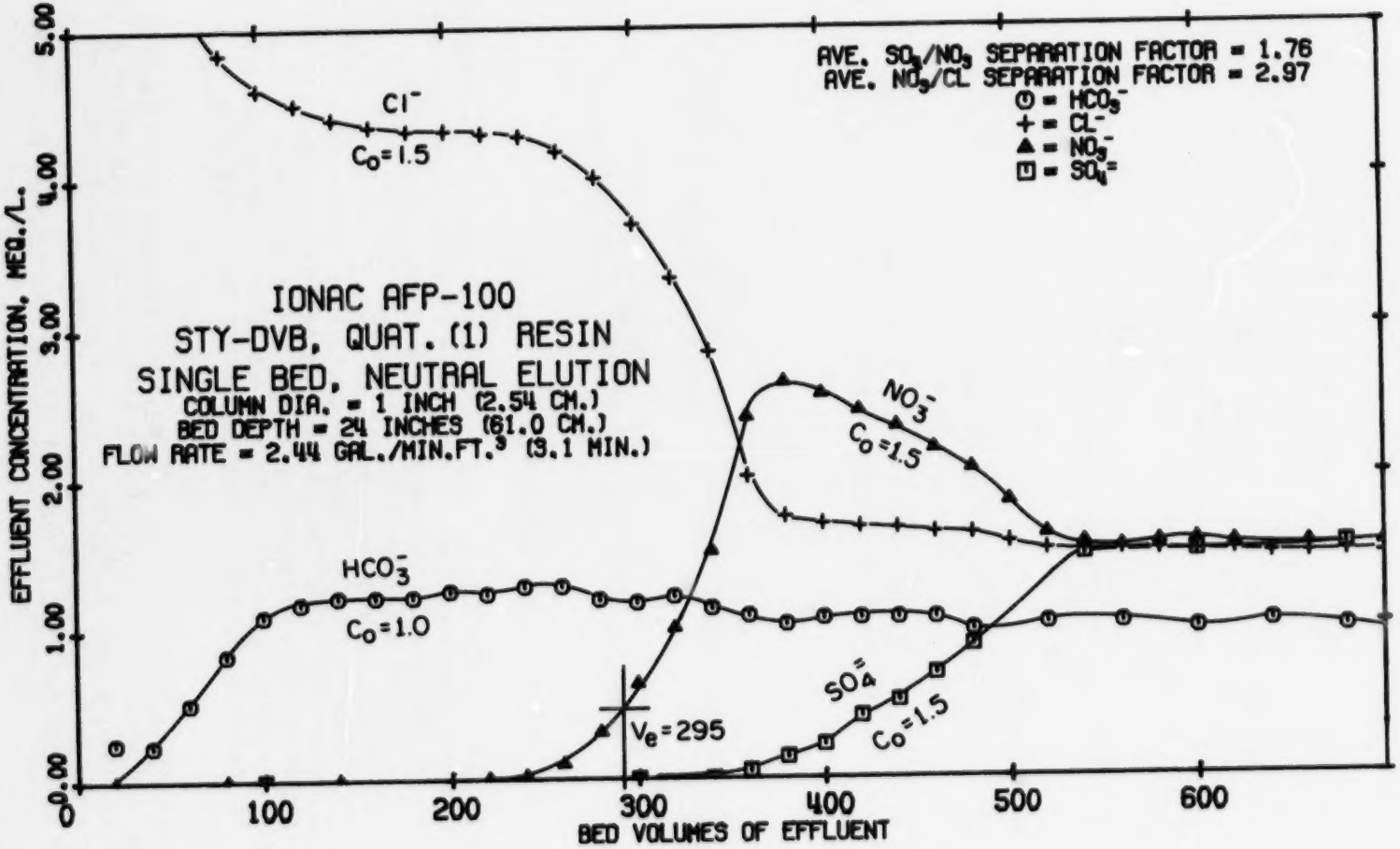


FIGURE 10
RUN NO. 7, EFFLUENT CONCENTRATION PROFILE

MEASURES OF EFFICIENCY

Maximum possible chemical efficiency (E_M) has been defined simply as $\bar{y}_N$ the average equivalent fraction of nitrate on the resin at the end of the run. Since y_N, the equivalent fraction of nitrate on the resin, varies with distance into the bed, the weighted average value ($\bar{y}_N$) must be used to represent the ratio of nitrate removed to all ions removed. In the ideally efficient process this would of course approach 1.0 which would only be possible if nitrate were much preferred over all other anions, and it was not in these experiments.

$$E_M = \bar{y}_N = \frac{\text{meq } NO_3^- \text{ on resin at end of run}}{\text{Total meq of ions on resin at end of run}}$$

$$E_M = \frac{\text{meq } NO_3^- \text{ in - meq } NO_3^- \text{ out}}{\text{Initial meq of all ions on resin + meq of all ions in -meq of all ions out}}$$

Overall chemical efficiency (E_0) is the product of the maximum possible chemical efficiency (E_M) and the observed regeneration efficiency (E_R).

$$E_0 = E_M E_R$$

$$E_R = \text{Regeneration Efficiency} = \frac{\text{meq total capacity of anion bed}}{\text{meq anion regenerant applied}}$$

$$E_0 = \text{Overall Chemical Efficiency} = \frac{\text{meq } NO_3^- \text{ removed}}{\text{meq anion regenerant applied}}$$

HOW SELECTIVITY EFFECTS COLUMN PERFORMANCE

Nitrate/Chloride selectivity ($\alpha_{N,Cl}$) is the most important selectivity in determining the relative amount of nitrate on the resin at nitrate breakthrough, i.e., in determining the maximum possible chemical efficiency ($E_M = \bar{y}_N$). This is both good and bad: good because all the resins were nitrate selective with respect to chloride, bad because little variation existed in the values of ($\alpha_{N,Cl}$) among the thirty-two resins tested ($\alpha_{N,Cl}$ = 1.85 - 4.33) and no real significant effects on selectivity seem possible by further manipulating those variables which were found to be most influential in the determination of $\alpha_{N,Cl}$, i.e., matrix and relative degree of cross-linking as indicated by porosity. Reasons for the importance of $\alpha_{N,Cl}$ are discussed below.

Sulfate/nitrate selectivity $\alpha_{S,N}$ is nearly irrelevant in determining the average equivalent fraction of nitrate on the resin at the end of a run ($\bar{y}_N$). Surprisingly, slight increases in $\bar{y}_N$ are possible as a result of increasing rather than decreasing the sulfate selectivity--$\alpha_{S,N}$. The explanation proposed for this is that (1) all the sulfate will be removed

from the feedwater regardless of its actual selectivity because it is the most preferred species and (2) high sulfate selectivity promotes a short sulfate-rich zone near the column entrance in which almost no nitrate is removed thereby leaving essentially all of that species to compete with the lesser preferred chloride in the second equilibrium zone of the column which is where nearly all of the nitrate is concentrated; see Figures 3 & 4. The inevitability of sulfate removal in the first enriched zone of the bed and the major nitrate--chloride competition in the second enriched zone of the bed are the reasons why the nitrate/chloride selectivity is the most important one to be considered. If either a strong or weak-base anion column is operated to nitrate breakthrough, that breakthrough will occur when the second enriched zone, containing primarily nitrate and chloride, reaches the outlet of the bed. The higher the nitrate/chloride selectivity is (measured here by $\alpha_{N,Cl}$) the higher will be the ratio of nitrate to chloride in the exhausted bed, and the greater will be $\bar{y}_N$, the maximum possible chemical efficiency.

Regardless of the explanation given, the effect of the selectivity of the most preferred species, sulfate, is predictably slight when the objective is to remove nitrate, invariably a less-preferred species. That is graphically demonstrated by the results from Runs 5 & 6 in Figure 11 where the sulfate/nitrate selectivity varies from 2.83 to 94 with no effect on the maximum possible chemical efficiency or on the throughput--a normalized measure of the equivalents of ions fed to the bed per equivalent of bed capacity.

THE EFFECT OF FEEDWATER NITRATE CONCENTRATION

The most important influence on the average amount of nitrate on the exhausted resin ($\bar{y}_N$) is, predictably, x_N the equivalent fraction of nitrate in the feed water; when it's low, process efficiency will be correspondingly low because the exhausted resin will comprise mostly sulfate and chloride--species not intended to be removed. In these studies the influence of x_N at 2.5 gal/min ft^3, $\alpha_{N,Cl}$ = 3.9 and x_S = 0.3 is shown in Table 3. Relative efficiency has been included in that table to illustrate that $\bar{y}_N$ is not simply a multiple of x_N.

TABLE 3. EFFECT OF NITRATE CONCENTRATION OF FEEDWATER

Equivalent Fraction of Nitrate Feed Water x_N	Average Equivalent Fraction of Nitrate on Spent Resin	Relative Efficiency
.20	.34	1.70
.27	.40	1.48

EFFECTS OF BED DEPTH, DETENTION TIME, AND SULFATE CONCENTRATION ON EFFICIENCY

In addition to $\alpha_{N,Cl}$ and x_N, the interrelated variables--service flow rate, bed depth and superficial detention time (τ), are quite significant.

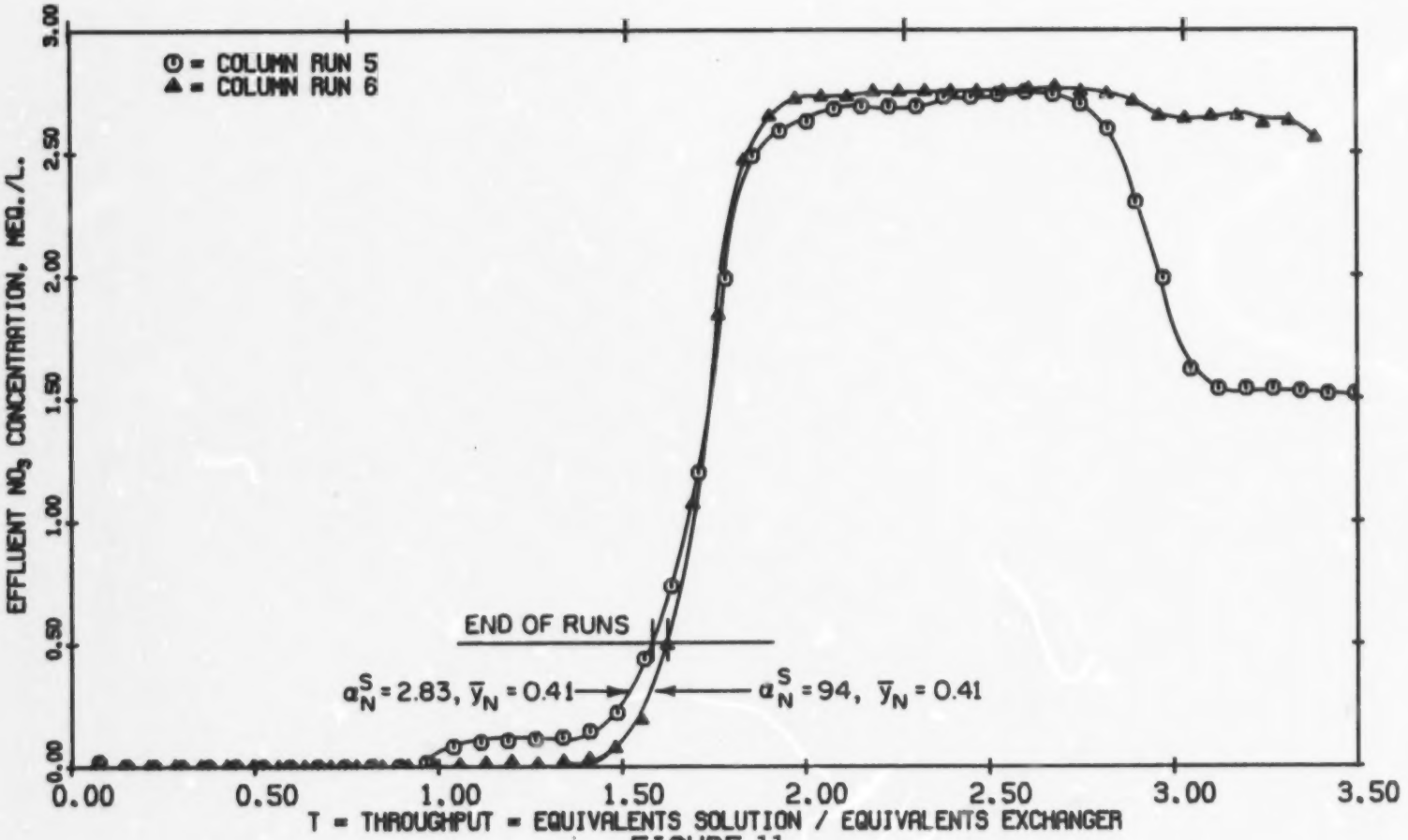


FIGURE 11
COLUMN EFFLUENT PROFILES (NITRATE)
EFFECT OF SULFATE SELECTIVITY ON COLUMN EFFICIENCY

Short detention times (τ < 3.0 min.), shallow beds (depth < 60 cm) and high service flow rates (> 2.5 gal/min ft^3) reduce $\bar{y}_N$ by causing relatively more chloride, apparently the kinetically favored anion, to be on the resin at nitrate breakthrough. Indications are that the detrimental effect is greater with microporous compared to macroporous resins and with high capacity compared to low capacity resins. These observations are derived from the data in Table 4 which compares the nitrate efficiencies ($\bar{y}_N$'s) of three different resins in shallow beds (τ = 1.5 min) and deep beds (τ = 3.0 min).

TABLE 4. EFFECT OF BED DEPTH AND SERVICE FLOW RATE

Resin	Resin Porosity	Capacity meq/ml	Service Flow Rate (gal/min ft^3)	Detention Time τ (min)	Resin Depth (cm)	$\bar{y}_N$
WGR	Micro	1.5	4.88	1.5	30.5	.36
ES-374	Macro	2.6	4.88	1.5	30.5	.36
ES-374	Macro	2.6	2.44	3.1	61.0	.41
ES-368	Macro	1.4	4.88	1.5	30.5	.39
ES-368	Macro	1.4	2.44	3.1	61.0	.41

Although x_S, the equivalent fraction of sulfate in the feed water) was not a variable in the column experiments, it will greatly influence $\bar{y}_N$ because all the sulfate fed to the column will be on it at nitrate breakthrough. When x_S is high, the efficiency, $\bar{y}_N$, will be low.

THE EFFECT OF REGENERATION STOICHIOMETRY ON EFFICIENCY

Because we are advocating the operation of the anion bed to a point considerably beyond exhaustion, the cation bed must not contain exchangeable hydrogen ions after the anion bed is exhausted. If it contains these excess hydrogen ions, they will be added to the cation bed effluent water but will not be removed or neutralized in the anion bed. On the other hand, if the cation bed doesn't contain a sufficient number of exchangeable hydrogen ions, it will breakthrough first and the potential capacity of the anion bed will not be realized to the detriment of process efficiency. For these reasons the capacities of the beds must be matched as closely as possible. In actual practice this will prove to be somewhat difficult because of the variable nature of the ion-exchange capacities of the beds. The ion-exchange capacity of the cation bed is a function of the cationic composition of the feedwater and the regeneration level, the latter being a measure of the quantity of regenerant applied compared to the stoichiometric amount theoretically required. The weak-base anion bed capacity is predominantly a function of the anionic composition of the feedwater and is not much influenced by the regeneration level because of the resin's great affinity for the regenerant hydroxide ions, i.e., its strong preference for the free-base form.

Regeneration level influences both the overall chemical efficiency (E_O) and the maximum possible chemical efficiency (E_M or $\bar{y}_N$). It has been determined here that a downflow regeneration level of 240-300% of the theoretical HCl required should be applied to the cation bed if calcium and magnesium are the primary cations on the resin; see simulated ground water composition in Table 2. Regeneration levels lower than 300% caused premature cation breakthrough, increasing pH, and reduced anion bed capacity with smaller values of $\bar{y}_N$ at breakthrough; see Runs 9 and 10, Table 5. In order to study the elution behavior of the anions under true ion-exchange conditions in the absence of a significant concentration of hydroxide ions, the capacity of the cation bed used in Runs 1-6 was deliberately made much larger than the capacity of the weak-base anion bed. By observing the minimum and final pH's of these runs in Table 5, the acidic nature of the system effluent during elution to nitrate breakthrough is evident for the case of cation bed capacity greater than anion bed capacity. In actual practice, the beds will have to be sized based on the resins chosen and the ground water composition. The efficiency of the regeneration operation should remain constant as long as the composition of the feedwater doesn't change drastically and the resins do not become fouled with organics, iron, or silica.

For the single-bed strong-base anion process regenerated with NaCl it is expected that a regeneration level of 300% or greater will be required for efficient regeneration. This is based on published rather than experimentally determined information [1].

The overall chemical efficiency (E_O) for waters similar to the test water in Table 2 can be expected to be about 13.3% for both the single-bed and two-bed processes. This estimate is based on operation to nitrate breakthrough with the observed average equivalent fraction of nitrate on the resin at the end of the runs ($\bar{y}_N = 0.40$) utilizing a feedwater containing the same equivalent concentrations of nitrate, chloride and sulfate with an irrelevant amount of bicarbonate which undergoes no net removal in either process. Higher equivalent fractions (x_N's) of nitrate in the feedwater will increase E_O and lower equivalent fractions will reduce it.

COST COMPARISONS FOR THE SINGLE-BED AND TWO-BED PROCESSES

A comparative economic evaluation of the processes reveals that the two-bed process with HCl and NH_4OH as regenerants has chemical plus disposal costs which are approximately 50% higher than the single-bed process if the following assumptions are made: an overall chemical efficiency of 13.3%, 25% bypass water, a feedwater with the composition of the test water in Table 2, NaCl-$NaNO_3$ brine disposal by trucking 8 miles before discharging into a stream, and no disposal costs for the high-nitrogen content wastewaters from the two-bed process which are given away for their fertilizer value. Considering only the chemical costs for regenerants, the two-bed process costs three times as much to operate as the single-bed process but yields nitrate free, partially softened water and a land disposable regenerant with fertilizer value. See Table 6 for cost details and chemical compositions of regenerants, and Table 7 below for the comparative costs of possible regenerants to remove 1 lb. equivalent of nitrate, i.e., 14 lbs. of N or 62 lbs. of NO_3^- ion.

TABLE 5: COLUMN PERFORMANCE CHARACTERISTICS

Run No.	* Flow $\frac{gal}{min.ft^3}$	Minimum pH / Final ph	Bed Depth cm	Resin Description (Cation Regeneration Level)	α^S_N	α^N_{Cl}	$\bar{y}_{Cl}$	$\bar{y}_S$	$\bar{y}_{HCO_3}$	$\bar{y}_N$	** Final Column Capacity meq/ml	† Ve BV
1	2.34	2.5 / 2.5	63.5	Duolite ES-368 STY-DVB, Tert-Amine, MR	2.83	3.87	.13	.53	.00	.34	1.65	582
2	4.88	2.5 / 2.5	30.5	Duolite ES-374 Polyacrylic, Polyamine, MR	94.	3.85	.26	.36	.02	.36	2.93	720
3	4.88	2.4 / 2.4	30.5	Duolite ES-368 STY-DVB, Tert. Amine, MR	2.83	3.87	.20	.40	.01	.39	1.36	364
4	4.88	2.5 / 2.5	30.5	Dowex WGR Epoxy-Amine, Polyamine, Gel	137.	1.99	.27	.37	.00	.36	1.62	391
5	2.44	2.4 / 2.4	61.0	Duolite ES-368 STY-DVB, Tert. Amine, MR	2.83	3.87	.16	.43	.00	.41	1.48	423
6	2.44	2.3 / 2.5	61.0	Duolite ES-374 Polyacrylic, Polyamine, MR	94.	3.85	.15	.44	.00	.41	3.12	920
7	2.44	6.1 / 7.4	61.0	Ionac AFP-100 STY-DVB, Quat.(I)Amine, MR	1.76	2.97	.14	.43	.01	.42	1.03	295
8	2.88	2.8 / 5.8	61.0	Duolite ES-368 (600%) STY-DVB, Tert. Amine, MR	2.83	3.87	.21	.40	.00	.39	1.39	375
9	2.44	4.5 / 6.7	61.0	Duolite ES-368 (120%) STY-DVB, Tert. Amine, MR	2.83	3.87	.31	.34	.02	.33	0.84	190
10	2.44	4.6 / 6.3	61.0	Duolite ES-368 (240%) STY-DVB, Tert. Amine, MR	2.83	3.87	.14	.44	.00	.42	1.15	334
11	2.44	4.7 / 5.5	61.0	Amberlite IR-45 (300%) STY-DVB, Polyamine, Gel	12.7	3.89	.08	.45	.03	.44	1.61	480

* $\frac{1}{gal/min.ft^3} \times 7.48$ = Superficial detention time, τ, minutes

† Ve = Bed volumes of effluent to 0.5 meq/l NO_3-breakthrough (end of run)

** Final Column Capacity is greater than measured HCl capacity because resin has higher capacity for sulfate which occupies a significant fraction of the available sites at the end of the run.

Final pH refers to the pH of the system effluent at nitrate breakthrough.

Minimum pH was the minimum pH observed during the course of the run.

TABLE 6: ECONOMIC AND REGENERANT WASTEWATER COMPARISONS BETWEEN THE SINGLE-BED AND TWO-BED PROCESSES

Item	Single-Bed Process	Two-Bed Process
Regenerant Chemical Costs, ¢/1000 gal H_2O Supplied. . . .	9.2	27.8
Regenerant Chemical Costs, ¢/m^3 H_2O Supplied	2.43	7.34
Regenerant Disposal Costs, ¢/1000 gal H_2O Supplied . . .	9.2	Nil
Regenerant Disposal Costs, ¢/m^3 H_2O Supplied	2.43	Nil
Regenerant plus Disposal Costs, ¢/1000 gal H_2O	18.4	27.8
Regenerant plus Disposal Costs, ¢/m^3 H_2O Supplied	4.86	7.34
Regenerant Volume, % Total Water Supplied	0.78	1.73
Regenerant Composition: Total Concentration, N	1.08	0.650
Total Dissolved Solids, ppm	69,200	37,400
Undesirable Cation (Na^+), ppm	24,900	0
Calcium ion, ppm	0	2,480
Magnesium ion, ppm	0	465
Ammonium ion, ppm	0	8,780
Sulfate ion, ppm	7,870	3,540
Nitrate ion, ppm	8,960	4,030
Chloride ion, ppm	27,500	18,100
Nitrogen, ppm	2,020	7,740
Nitrogen Fertilizer Produced, lb N/1000 gal H_2O Supplied	0	1.12
Nitrogen Fertilizer Produced, kg/m^3 H_2O Supplied	0	.134
Per capita Fertilizer Production, lb N/capita·year . . .	0	40.9
Per capita Fertilizer Production, kg N/capita·year . . .	0	18.6

TABLE 7: CALCULATED CHEMICAL REGENERANT COSTS

Regenerant Chemical	$ / lb-equivalent*	¢ / 1000 gal supplied**	¢ / m^3 supplied**
H_2SO_4	1.23	8.63	2.28
NaCl	1.30	9.15	2.42
NH_3	1.53	10.7	2.78
HCl	2.43	17.1	4.52
NH_4Cl	5.64	39.6	10.5
HNO_3	6.62	46.5	12.3

* 1 lb-equivalent = 14 lbs of nitrogen or 62 lbs of nitrate

**Assumes regeneration level of 300%, 25% bypass and $\bar{y}_N = 0.40$

Note that the cost estimates in Table 6 include only chemical and disposal costs. They do not include capital costs for plant and equipment, depreciation, labor, interest, or pumping costs. Clearly these excluded costs are a significant portion of the total cost of supplying potable water of acceptable nitrate concentration but these items were not the objectives of this study and consequently no detailed calculations of them were made. Nevertheless, one can obtain conservative "ball-park" estimates of the total costs by doubling the 1970 amortization, power, labor, and maintenance costs given by Holzmacher [13] and adding that figure to the chemical plus disposal costs calculated here. This results in very rough estimates of 37¢/1000 gal for the single-bed process with regenerant disposal, and 55¢/1000 gal for the two-bed process with the regenerants given away, and further estimating that amortization, power, labor, and maintenance are 150% of the single-bed process. Holzmacher's system included 4 MGD of installed, continuous ion-exchange capacity operated 40% of the time. Again, as a rough estimate, we might conclude that treating a water containing approximately 400 mg/l TDS and 21 mg/l nitrate nitrogen by ion exchange is going to add between 37¢/1000 gal and 55¢/1000 gal to the cost of the water delivered to the distribution system if the cost of regenerant disposal is considered. If we neglect this disposal cost, the single-bed process can probably be operated in 1977 at a total added cost of 28¢/1000 gal of water supplied. These "ball-park" estimates are also subject to the assumptions of 25% bypass water, downflow regeneration with 300% of the theoretical requirement, and an exhausted resin which is 40% in the nitrate form at nitrate breakthrough.

SECTION 7

DESIGN CONSIDERATIONS FOR WATER SUPPLY APPLICATIONS

THE USE OF NITRIC ACID

Nitric acid is definitely not recommended as a regenerant in the two-bed process even though it would greatly enhance the fertilizer value of the regenerant wastewaters. Nitric Acid is too costly, 46.5¢/1000 gal water supplied (12.3¢/m^3), requires excess cation bed rinsing to reduce the residual nitrate concentration, and allows the possibility of disastrous nitrate and acid pollution of the water supply in the event of an operating error. Even though HCl is more costly than H_2SO_4 it may be more economical where large excesses of H_2SO_4 are required due to $CaSO_4$ fouling of the cation bed. Where H_2SO_4 can be used, however, it should be used because of its lower cost. Refer to Table 7 for a cost comparison of regenerants for both cation and anion beds.

ORGANIC EXTRACTABLES LEACHED FROM THE RESINS

Even after conditioning by extensive backwashing followed by two complete exhaustion-regeneration cycles including the usual backwashes and rinses, all the anion resins tested continued to bleed measurable amounts of organics into the treated water. The organic extractables leached from these conditioned resins gave rise to total organic carbon (TOC) concentrations in the 3--90 ppm range in acidic aqueous solutions containing about 1.0 weight % resin tumbled at 13 rpm for 16--20 hours; see Table 8 below.

TABLE 8: ORGANICS LEACHED BY AGITATING CONDITIONED ANION RESINS

Resin	Description	PPM TOC
3	STY-DVB, Weak Base	35
2	Acrylic-Amine, Weak Base	5
6	Phenol-HCHO, Weak Base	26
11	Aliphatic-Amine, Weak Base	90
7	Epoxy-Amine, Weak Base	25
16	STY-DVB, Strong Base	6

1% Resin Solutions Tumbled 16 Hours at 25°C

The leached organics are primarily non-volatile at 100°C. This is indicated in Table 9 which is a listing of the volatile (VOC) and non-volatile carbon (NVOC) analyses of the supernatants from conditioned resins left standing approximately six months in distilled water at room temperature. Some of these organic carbon concentrations are alarmingly high especially in light of the recent interest in low levels of organics in water supplies as precursors to carcinogens formed upon reaction with chlorine. This problem definitely merits further investigation.

TABLE 9: ORGANICS LEACHED FROM CONDITIONED IX RESINS UPON STANDING

Resin	Description	PPM VOC	PPM NVOC
3	STY-DVB, Weak Base	10	182
6	Phenol-HCHO, Weak Base	12	137
11	Aliphatic-Amine, Weak Base	3	3870
7	Epoxy-Amine, Weak Base	47	520
16	STY-DVB, Strong Base	3	61
C-1	STY-DVB, Strong Acid	3	428

50% Resin Solutions Standing 6 Mos. at 25°C

A DEGASIFIER TO REMOVE CO_2

In the two-bed system, the first species to be eluted is carbonic acid (H_2CO_3) at which time the pH of the treated water drops to approximately 4.5. This acid gas (CO_2) must of course be removed before permitting the treated water to enter the distribution system. Usually, in such a two-bed system, a degasifier would be installed between the cation and anion beds to remove CO_2 under the very acidic conditions produced by the mineral acids present at that point. This may not be good practice in systems where it is desired to operate to nitrate breakthrough. A better location may well be following rather than preceding the weak-base anion bed. Some beneficial kinetic effect due to the presence of H_2CO_3 in column experiments was observed during the course of the experimental work and reported elsewhere (I. Abrams, Diamond Shamrock Chemical Co., Personal Communication). Apparently, in column operation, H_2CO_3 is neutralized by the weak-base resin, whereupon the HCO_3^- anions are taken up thereby swelling the resin beads in the lower reaches of the bed where they compete with no other anion; finally the swollen, bicarbonate-form resin takes up the next most preferred species (chloride) by rapidly exchanging the HCO_3^- for it. Simply stated, the bicarbonate anion is a catalyst for the removal of the more preferred species in ion-exchange column operations. Thus, it is questionable whether removing CO_2 from waters before anion-exchange in nitrate removal is good or bad design since the closer the approach to equilibrium, the more chemically efficient is the operation of this process.

RANKING THE STRONG- AND WEAK-BASE ANION RESINS

The recommended anion resins for nitrate removal service are listed in Table 10 considering that high nitrate/chloride selectivity high capacity, and moderate sulfate/nitrate selectivity are desirable characteristics. Organic extractables as evidenced by the TOC of resin equilibrates were not considered in making the rankings because of the very preliminary nature of those measurements. However, an asterisk (*) has been used to indicate a resin producing markedly colored water in addition to high TOC.

Although the resins are ranked in preference order, the differences among the recommended resins are not large; they are all expected to give nearly the same maximum possible chemical efficiency E_M. Some overall process efficiency is gained by using high capacity resins while some might be lost with the highly sulfate selective resins should they require large rinse volumes. Note that the rankings are not endorsements by the authors or the EPA of any of the resins listed.

TABLE 10: RANKING OF RESINS FOR USE IN NITRATE REMOVAL SERVICES

Recommended

STY-DVB, Polyamine, Resins
- Amberlite IR-45

STY-DVB, Tertiary-amine, MR Resins
- Amberlite IRA-93
- Dowex MWA-1
- Ionac AFP-329
- Duolite ES-368

STY-DVB, Quat. (I & II) Amines, Gel, MR and Improved Porosity Resins
- Ionac ASB-1, AFP-100, A-641, ASB-1P, ASB-2
- Duolite, A-101-D, A-102-D
- Dowex 11, SAR, SBR-P, SBR
- Amberlite IRA-400, IRA-900, IRA-402, IRA-910, IRA-410
- Ionac A-550, A-540 (No DVB crosslinking)
- Duolite A-104 (mixed Types I and II Amines)

Acrylic-Amine, Polyamine, MR Resins
- Duolite ES-374

Phenol-HCHO, Polyamine, MR Resins
- Duolite A-7
- Duolite ES-561

Not Recommended

Epoxy-amine, Polyamine, Gel Resins
- Dowes WGR
- Duolite A-340
- Ionac A-305

Acrylic-Amine, Tertiary Amine, Gel Resins
- Amberlite IRA-68

Aliphatic-Amine Polyamine, Gel Resins
- *Ionac A-260

REFERENCES

1. Beulow, R. W., K. L. Kropp, J. Withered, and J. M. Symons, "Nitrate Removal by Anion Exchange Resins," Water Supply Research Laboratory, National Environmental Research Center, U.S. EPA, Cincinnati, Ohio, May, 1974.

2. Bingham, E. C., "Fertilizer Maker Stops Nitrogen," Water and Wastes Engineering, P.E.-4, November, 1972.

3. Boari, G., L. Liberti, C. Merli, and R. Passino, "Exchange Equilibria on Anion Resins," Desalination, V. 15, p. 145-166 (1974).

4. Clifford, Dennis A., "Nitrate Removal from Water Supplies by Ion Exchange: Resin Selectivity and Multicomponent Chromatographic Column Behavior of Sulfate, Nitrate, Chloride, and Bicarbonate," Ph.D. Thesis, University of Michigan, University Microfilms, Ann Arbor, Michigan, Pub. No. 77-7893 (1976).

5. Diamond Shamrock Chemical Co., Duolite Ion-Exchange Manual, Redwood City, CA (1969).

6. Dorfner, K., Ion Exhchangers: Properties and Applications, 3rd. Ed., Ann Arbor Science, Ann Arbor, Mich. (1972).

7. Evans, S., "Nitrate Removal by Ion-Exchange," J. WPCF, V. 45, No. 4, pp. 632-36, April, 1973.

8. Gauntlett, R. B., "Nitrate Removal from Water by Ion-Exchange," Water Treatment and Examination, V. 24, p. 172 (1975).

9. Gregg, J. C., "Nitrate Removed at Water Treatment Plant," Civil Engineering - ASCE, p. 45, April, 1973.

10. Helfferich, Friedrich, Ion-Exchange, McGraw-Hill Book Co. Inc., New York, N.Y. (1962).

11. Helfferich, F. G., "Multicomponent Ion Exchange in Fixed Beds," I & EC Fund., V. 6, No. 3, p. 362 (1967).

12. Helfferich, F. and G. Klein, Multicomponent Chromatography: Theory of Interference, Marcel Dekker, New York (1970).

13. Holzmacher, R. G., "Nitrate Removal from a Ground Water Supply," Water and Sewage Works, p. 210, July, 1971.

14. Klein, G., D. Tondeur, T. Vermeulen, "Multicomponent Ion Exchange in Fixed Beds," I & EC Fund., Vol. 6, No. 3, p. 339 (1967).

15. Kunin, R., Ion Exchange Resins, 2nd Ed., John Wiley & Sons Inc., New York (1958).

16. Midkiff, W. S. and Weber, W. J., Jr., "Operating Characteristics of Strong-Base Anion Exchange Reactors," Proceedings of the 25th Purdue Industrial Waste Conference, May, 1970.

17. National Academy of Sciences, "Summary Report: Drinking Water and Health," National Academy of Sciences, Washington, D. C., 1977.

18. Tondeur, D. and G. Klein, "Multicomponent Ion-Exchange in Fixed Beds," I & EC Fund., V. 6, No. 3, p. 351, August, 1967.

19. U. S. EPA, "Interim Primary Drinking Water Standards," Federal Register, December 24, 1975.

GLOSSARY

"as $CaCO_3$": Normality (N) can be converted to calcium carbonate equivalents. There are 50 mg of $CaCO_3$ per millequivalent. Any 0.005 N solution contains 5 milliequivalents/l or the equivalent of 250 mg/l of $CaCO_3$.

bed: The ion-exchange resin contained in a column. Water to be treated by ion-exchange is passed downward through the column.

breakthrough: The appearance of a sharp increase in the concentration of an ion in the effluent from the bed.

capacity: The total number of ion-exchange sites available per unit volume of resin measured in equivalents/l or milliequivalents/ml. Resins were equilibrated with 0.005 N acids (HCl, H_2SO_4 or HNO_3) for the experimental capacity determinations. This was done to simulate the expected capacities in typical groundwater applications.

chromatographic elution: Continued application of the feed water to an exhausted ion-exchange bed so as to "elute" or sequentially drive off those less-preferred feed water anions previously removed during the exhaustion cycle. In this operation, the ions being driven off the resin are separated into zones in which the aqueous concentration of the primary ion in a given zone exceeds the concentration of that ion in the feed water.

downflow regeneration: Cocurrent regeneration, i.e., the regenerant solution is passed down through the bed in the same direction as the feed water was passed through the bed.

effluent profile: A plot of the effluent concentration of an ion or ions vs. the volume of effluent water from the bed.

elution: The displacement of non-preferred ions previously removed from the feed water by continued application of the feed water or an "eluting solution" containing an ion or ions more preferred by the ion exchanger.

equivalent: One gm equivalent (6.023×10^{23}) of ionic charges in the aqueous phase or that number of fixed charges in the resin phase.

equivalent fraction: That fraction of the total negative or positive charges present which is due to a given ion. If $x_S = 0.27$, then 27% of the negative ionic charges in a given volume of water are due to sulfate ions.

exhaustion: The step in an ion-exchange cycle in which the undesirable ions are removed from the water being treated. The resin bed is said to be "exhausted" when the ions originally on the resin have been essentially completely exchanged for feed water ions.

functionality: A description of the nature of the amine groups attached to the resin matrix which give an anion resin its ion exchange properties, e.g., quaternary amine functionality.

ion-exchange: A physicochemical process in which ions in the water being treated replace and are exchanged for ions in a solid phase (the resin). In the single-bed process, nitrate, the pollutant ion, is placed on the resin phase in exchange for an innocuous ion such as chloride.

isoporous resins: Resins having slightly greater uniform porosity than typical microporous resins.

isotherm: A constant temperature plot of resin phase concentration of an ion vs. the water phase concentration of that ion. In a binary isotherm, e.g., sulfate/nitrate, the resin phase exchange sites not occupied by sulfate are occupied by nitrate. Similarly, the significant anions in the water which are not sulfate are nitrate.

macroporous resins (also referred to as macroreticular resins): Very porous resins whose beads comprise aggregates of gel resins with large internal voids having diameters up to several hundred angstroms (A). This porosity is non-uniform with areas of very high crosslinking. Macroporous resin beads are opaque.

matrix: The polymer backbone of a synthetic organic ion-exchange resin.

microporous resins (also referred to as gel resins): resins with porosity of atomic dimensions, i.e., having "pores" which are 10-20 A in diameter. Gel resins are relatively uniform in porosity and the beads are transparent.

milliequivalent: (Abbreviated meq.) 1/1000 of an equivalent. An 0.005 N solution contains 0.005 equivalents/l or 5 meq/l.

porosity: A measure of the degree of openness of the polymer matrix which is related to the nature and degree of crosslinking.

regeneration: The displacement from the exhausted ion-exchange resin of the undesirable ions removed from the water during the exhaustion cycle. Performed by passing through the bed, a relatively concentrated (1 N) solution of the ion desired on the resin.

regeneration level: A measure of the inefficiency of regeneration expressed here in %. The level indicates the amount of regenerant which must actually be applied compared to the amount theoretically required. For downflow regeneration a level of 300% is typically required; that means a 200% excess of regenerant must be applied.

selectivity: A measure of the relative affinity for one ion over another exhibited by the resin. In this report selectivity (relative affinity) is measured by the separation factor, α. This α should not be confused with the selectivity coefficient, K.

selectivity sequence: A listing of ions as preferred by the ion exchanger ordered from most preferred to least preferred.

separation factor (binary): The ratio of the distribution of ions between the water phase and the resin phase. $\alpha_{S,N}$ is the ratio of the distribution of sulfate ions between phases to the distribution of nitrate ions between phases. If $\alpha_{S,N} \geq 1$, the resin prefers sulfate over nitrate.

service flow rate: The rate of application of feedwater to the resin bed. Because the exchanger capacity is related to the volume of resin, the rate is usually specified as gal/min ft^3 or volume of feed water per volume of resin per unit time. With proper units this is reciprocal superficial detention time. Recommended exhaustion rates are 1-5 gal/min ft^3 corresponding to detention times of from 7.48 to 1.50 minutes.

softening: In ion exchange, a process by which polyvalent cations, e.g., calcium, magnesium, and iron are exchanged for a monovalent cation such as hydrogen or sodium.

spent regenerant: A wastewater containing the excess regenerant ions and the undesirable ions removed from the exhausted resin. Its volume will be determined by the volume of rinses included as "spent regenerants."

strong-base resin: An anion exchange resin containing fixed positively charged quaternary amine functional groups which prefer all common anions over hydroxide ions. Simply, a resin which tends to readily give up hydroxide ions in exchange for nearly any other anion. The capacity of strong-base resins to exchange ions does not depend on the presence of excess hydrogen ions (acidity) to form the positively charged exchange sites as is the case with weak-base resins. Thus, they may be used as ion exchangers in acid, neutral, and basic solutions.

superficial detention time (τ): The time a particle of feed water spends in the empty resin bed assuming plug flow. It is calculated as the empty bed volume divided by the feed flow rate.

upflow regeneration: Countercurrent regeneration, i.e., the regenerant solution is passed up through the bed in a direction opposite to that taken by the feedwater. Countercurrent regeneration is reportedly more efficient than cocurrent regeneration because the most preferred ions are not driven through the entire bed.

weak-base resin: An ion-exchange resin comprising primary, secondary, or tertiary amine functional groups or a mixture of those groups which acquire positive charges when excess hydrogen ions (acidity) are present. These charged sites can exchange anions if the feed solution remains acidic. Thus, these resins are said to "adsorb" acids. In neutral to

basic solutions they have no charged sites and consequently no significant anion exchange capacity. They are readily regenerated with weak bases or even neutral water solutions.